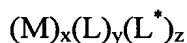
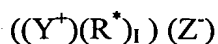


thermally stable solid in reaction media, having a mean pore diameter in the range of about 3-3000 Å and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}^-$ ; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}$ , y is at least 1,  $\text{L}^*$  is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene,  $=\text{C}$ : having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7 and the quaternary ammonium compound has a general formula



wherein,  $I = 4$  for  $Y^+ = N^+, P^+, As^+$ ;  $I = 3$  for  $Y^+ = S^+$  and  $R^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, aryloxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-SO_3^-$ ,  $-SO_2^-$ ,  $-PO_3^{2-}$ ,  $-COO^-$ ,  $-O^-$ ,  $AsO_3^{2-}$  and  $-S^-$  and  $Z$  is anion selected from organic anion, inorganic anion or coordination complex anion, and the group IIA metal cation are selected from compounds of  $Ca^{2+}$ ,  $Sr^{2+}$  and  $Ba^{2+}$ . --

-- 89. A process as claimed in claim 88 is carried out in the temperature ranging from  $-70$  to  $200^{\circ}C$  preferably between  $-5$  to  $100^{\circ}C$ . --

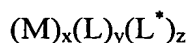
-- 90. A process as claimed in claim 88 wherein, the solvent is aqueous, water miscible organic or mixture thereof. --

-- 91. A process as claimed in claim 88 wherein, the support having deposited thereon catalytically active entity and catalytically inert additive is added to a solution of group IIA metal compound, with simultaneous agitation over a period of 10 to 1500 min. --

-- 92. A process as claimed in claim 88 wherein, the catalyst is recovered by centrifugation, decantation, gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum. --

-- 93. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a catalytically active solid, said process is characterized by impregnation of support with a solution of a catalytically inactive additive and a catalytically active entity followed by drying and suspending the solid support having deposited thereon the catalytically inactive additive and the catalytically active entity in water immiscible solvent to which a solution of group IIA metal compound solution is added with vigorous agitation and concurrent removal of low

boiling or azeotropic fraction of solvent and the suspension is allowed to age for 1 to 48 hours, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 Å<sup>0</sup> and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>2-</sup>, -COO<sup>-</sup>, -O<sup>-</sup>, AsO<sub>3</sub><sup>2-</sup> and -S<sup>-</sup>; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>2-</sup>, -COO<sup>-</sup>, -O<sup>-</sup>, AsO<sub>3</sub><sup>2-</sup> and -S<sup>-</sup>, y is at least 1, L<sup>\*</sup> is radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy,

aryloxy, cycloalkyl, z is from 0 to 7, and quaternary ammonium compound has a general formula



wherein, I = 4 for  $Y^+ = N^+, P^+, As^+$ ; I = 3 for  $Y^+ = S^+$  and  $R^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, aryloxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-SO_3^-, -SO_2^-, -PO_3^{2-}, -COO^-, -O^-, AsO_3^{2-}$  and  $-S^-$  and Z is anion selected from organic anion, inorganic anion or coordination complex anion, the group IIA metal cation are selected from compounds of  $Ca^{2+}, Sr^{2+}$  and  $Ba^{2+}$ .

-- 94. A process as claimed in claim 93 is carried out in the temperature ranging from -70 to 200°C. --

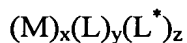
-- 95. A process as claimed in claim 93 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof. --

-- 96. A process as claimed in claim 93 wherein, the solvent employed is water immiscible organic solvent, having boiling point in the range 40 to 200 °C. --

-- 97. A process according to claim 93 wherein, the catalyst is recovered by centrifugation, decantation or gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum. --

-- 98. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of porous solid support having deposited thereon a group IIA metal compound followed by drying and suspending the solid support having deposited

thereon group IIA metal in water immiscible solvent to which a solution of catalytically active entity and catalytically inactive additive is added with vigorous agitation and concurrent removal of low boiling or azeotropic fraction of solvent and the suspension is allowed to age for 1 to 48 hours, wherein the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 3-3000 Å<sup>0</sup> and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}^{-1}$ ; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged

functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}^-$ , y is at least 1,  $\text{L}^*$  is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene,  $=\text{C}$ : having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and the quaternary ammonium compound has a general formula



wherein,  $I = 4$  for  $\text{Y}^+ = \text{N}^+$ ,  $\text{P}^+$ ,  $\text{As}^+$   $I = 3$  for  $\text{Y}^+ = \text{S}^+$  and  $\text{R}^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}^-$  and Z is anion selected from organic anion, inorganic anion or coordination complex anion and the group IIA metal cation are selected from compounds of  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ba}^{+2}$ .

-- 99. A process as claimed in claim 98 is carried out in the temperature ranging from  $-70$  to  $200^\circ\text{C}$ . --

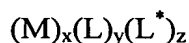
-- 100. A process as claimed in claim 98 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof. --

-- 101. A process as claimed in claim 98 wherein, the solvent employed is water immiscible organic solvent, having boiling point in the range  $40$  to  $200^\circ\text{C}$ . --

-- 102. A process as claimed in claim 98 wherein, the catalyst is recovered by centrifugation, decantation, gravity settling or other techniques of solid liquid separation and solids dried subsequently in vacuum. --

-- 103. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising fluidizing solid support in the current of gasses and spraying a solution of catalytically active entity and a catalytically inert additive in such a way that the catalytically active entity and the catalytically inert additive are deposited on the solid support, the fluidization of solid is continued for 1 to 48 hours and a solution of group IIA metal compound is subsequently sprayed and fluidization of solid is further continued for 1 to 48 hours and solids are recovered, wherein, the support is mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 Å<sup>0</sup> and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from

-SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>2-</sup>, -COO<sup>-</sup>, -O<sup>-</sup>, AsO<sub>3</sub><sup>2-</sup> and -S<sup>-</sup>; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl,

alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}$ , y is at least 1,  $\text{L}^*$  is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene,  $=\text{C}$ : having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and quaternary ammonium compound has a general formula



wherein,  $I = 4$  for  $\text{Y}^+ = \text{N}^+$ ,  $\text{P}^+$ ,  $\text{As}^+$ ;  $I = 3$  for  $\text{Y}^+ = \text{S}^+$  and  $\text{R}^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-\text{SO}_3^-$ ,  $-\text{SO}_2^-$ ,  $-\text{PO}_3^{2-}$ ,  $-\text{COO}^-$ ,  $-\text{O}^-$ ,  $\text{AsO}_3^{2-}$  and  $-\text{S}^-$  and Z is anion selected from organic anion, inorganic anion or coordination complex anion, the group IIA metal cation are selected from compounds of  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ba}^{+2}$ .

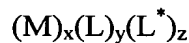
-- 104. A process as claimed in claim 103 is carried out in the temperature ranging from  $-70$  to  $200^\circ\text{C}$ . --

-- 105. A process as claimed in claim 103 wherein, the solvent employed to form a solution of group IIA metal ion is aqueous, water miscible organic or mixture thereof. --

-- 106. A process for the preparation of a heterogeneous catalytic formulation as a solid composite comprising of tumbling solid support in the rotating pan under current of gasses, a solution of catalytically active entity and a catalytically inert additive is sprayed in such a way that the catalytically active entity and the catalytically inert additive are deposited on the solid support, the tumbling of solid is continued for 1 to 48 hours and a solution of group IIA metal compound is subsequently sprayed and tumbling of solid is further continued for 1 to 48 hours and solids are recovered, wherein the support is



mechanically robust and thermally stable solid in reaction media, having a mean pore diameter in the range of about 70-3000 Å<sup>0</sup> and existing as powder, granules, flakes or pellets of regular or irregular shapes, sheets, monolith, ropes and woven fabric of fibrous solids and the catalytically inactive additive is independently selected from anions having at least two or more negative charges which may be organic, inorganic, or a compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>2-</sup>, -COO<sup>-</sup>, -O<sup>-</sup>, AsO<sub>3</sub><sup>2-</sup> and -S<sup>-</sup>; the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof, the metal complexes having a general formula



wherein M is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements, x is from 1 to 60, L is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from -SO<sub>3</sub><sup>-</sup>, -SO<sub>2</sub><sup>-</sup>, -PO<sub>3</sub><sup>2-</sup>, -COO<sup>-</sup>, -O<sup>-</sup>, AsO<sub>3</sub><sup>2-</sup> and -S, y is at least 1, L<sup>\*</sup> is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene, =C: having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl, z is from 0 to 7 and the quaternary ammonium compound has a general formula



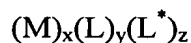
wherein,  $I = 4$  for  $Y^+ = N^+, P^+, As^+$ ;  $I = 3$  for  $Y^+ = S^+$  and  $R^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alkoxy, arlyoxy, cycloalkyl bearing at least one or more negatively charged functional groups independently selected from  $-SO_3^-$ ,  $-SO_2^-$ ,  $-PO_3^{2-}$ ,  $-COO^-$ ,  $-O^-$ ,  $AsO_3^{2-}$  and  $-S^-$  and  $Z$  is anion selected from organic anion, inorganic anion or coordination complex anion and the group IIA metal cation are selected from compounds of  $Ca^{+2}$ ,  $Sr^{+2}$  and  $Ba^{+2}$ . --

-- 107. A process as claimed in claim 106 is carried out in the temperature ranging from  $-70$  to  $200^{\circ}C$ . --

-- 108. A process as claimed in claim 106 wherein, the solvent employed to form solutions is aqueous, water miscible organic or mixture thereof. --

-- 109. A process as claimed in claim 106 wherein, the solutions are sprayed simultaneously or sequentially. --

-- 110. Use of a catalyst as claimed in claim 1 in a reaction wherein, the reaction is selected from analogous reactions that are catalyzed by catalytically active entity in liquid phase, the catalytically active entity is independently selected from metal complexes, quaternary compounds, metal oxo anions and polyoxometallates or combinations thereof such that metal complexes having a general formula



wherein  $M$  is catalytic metal atom or ion of coordination complex is a transition metal from group IIIB, IVB, VB, VIB, VIIB, IB or IIB of the periodic table of elements,  $x$  is from 1 to 60,  $L$  is aliphatic, aromatic and heterocyclic compounds containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene having attached thereto oxy, alkyl, aryl, arylalkyl,

alkylaryl, alcoxy, arlyoxy, cycloalkyl y is at least 1,  $L^*$  is a radical selected from organic anion, inorganic anion and coordinating compound containing at least one radical from O, N, S, Se, Te, P, As, Sb, Bi, Si, olefin, carbene,  $=C:$  having attached thereto oxy, alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl, z is from 0 to 7, and the quaternary ammonium compound has a general formula



wherein,  $I = 4$  for  $Y^+ = N^+, P^+, As^+$ ;  $I = 3$  for  $Y^+ = S^+$  and  $R^*$  is selected independently from alkyl, aryl, arylalkyl, alkylaryl, alcoxy, arlyoxy, cycloalkyl and  $Z^-$  is anion selected from organic anion, inorganic anion or coordination complex anion.